

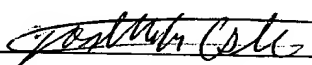


## DECLARATION

I, Japanese Patent Attorney Yoshitaka OSHIDA, having my office at GINZA BUILDING 3-12, 3-CHOME, GINZA CHUO-KU, TOKYO, JAPAN, do solemnly and sincerely declare:

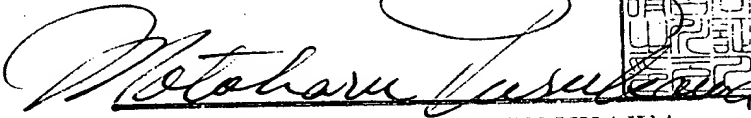
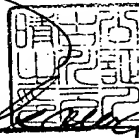
1. That I am well acquainted with the Japanese and English languages, and
2. That the attached document: Specification  
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And I make this solemn declaration conscientiously believing the same to be true and correct.

  
Yoshitaka OSHIDA

Affirmed before me

► May 13, 2004

Notary : MOTOHARU FURUKAWA  
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証

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平成16年 5 月 13 日、本公証人役場において

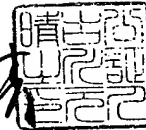
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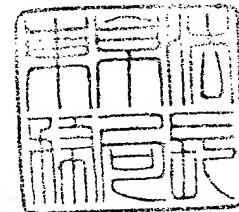
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平成16年 5 月 13 日

東京法務局長

石井政治



APOSTILLE

(Convention de La Haye du 5 octobre 1961)

1. Country: JAPAN

This public document

2. has been signed by MOTOHARU FURUKAWA

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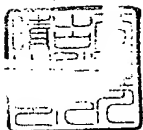
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Shinichi Hagiwara

Shinichi HAGIWARA

For the Minister for Foreign Affairs



## JAPAN PATENT OFFICE

This is to certify that the annexed is a true copy of the following application as filed with this office.

Date of Application: March 10, 1999

Application Number: JP1999-063099

Applicant(s): NEOMAX CO.,LTD.

May 7, 2004

Commissioner, Japan Patent Office: Yasuo IMAI

Certificate No. 2003-3038405

(Title of document)	Patent Application	
(File No.)	30P99009	
(Filing date)	MARCH 10, 1999	
To: Director-General of Patent Office :	Takeshi ISAYAMA	
(International Patent Classification):	HO1L 35/14 C10B 33/06	
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(Number of Note)	055918	
(Amount)	21000	
(List of Filing Documents)		
(Title)	Specification	1
(Title)	Drawings	1
(Title)	Abstract	1
(Number of General Power of Attorney)	9710264	
(Proof)	yes	

【Name of Document】 Specification

【Title of Invention】 THERMOELECTRIC CONVERSION MATERIAL,  
AND METHOD FOR MANUFACTURING THE SAME

【What is claimed is】

【Claim 1】 A thermoelectric conversion material comprising a laminate in which a silicon layer or a silicon-rich layer composed mainly of silicon and an added element-rich layer composed mainly of one or more added elements to make a silicon a p-type or n-type semiconductor are laminated and formed on a substrate or a film and comprising the entire composition wherein silicon contains said added element in an amount of 0.001 to 20 at%.

【Claim 2】 The thermoelectric conversion material according to claim 1, wherein a heat treatment is performed on a laminate.

【Claim 3】 The thermoelectric conversion material according to claim 1, wherein at least each one type of added elements (added elements  $\alpha$ ) to make a p-type semiconductor and added elements (added elements  $\beta$ ) to make an n-type semiconductor is contained in an amount of 0.002 to 20 at% in total amount, and the total amount of the added elements  $\alpha$  or  $\beta$  is contained by the amount required to make a p-type or n-type semiconductor over the total amount of the relative added elements  $\alpha$  or  $\beta$ .

【Claim 4】 The thermoelectric conversion material according to claim 1, wherein added elements to make a p-

type semiconductor (added elements  $\alpha$ ) are one or more types selected from each group consisting of added elements A (Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg, B, Al, Ga, In, Tl) and transition metal elements  $M_1$  (Y, Mo, Zr), and added elements to make an n-type semiconductor (added elements  $\beta$ ) are one or more types selected from each group consisting of added elements B (N, P, As, Sb, Bi, O, S, Se, Te), transition metal elements  $M_2$  (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Ru, Rh, Pd, Ag, Hf, Ta, W, Re, Os, Ir, Pt, Au; where Fe accounts for 10 at% or less), and rare earth elements RE (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu).

【Claim 5】 The thermoelectric conversion material according to claim 1, wherein Group III - V compound semiconductors or Group II - VI compound semiconductors are contained in an amount of 1 to 10 at%, and further at least one type of the added elements A (Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg, B, Al, Ga, In, Tl) or the added elements B (N, P, As, Sb, Bi, O, S, Se, Te) is contained in an amount of 1 to 10 at%.

【Claim 6】 The thermoelectric conversion material according to claim 1, wherein at least one type of Ge, C and Sn is contained in an amount of 0.1 to 5 at%, and one or more types selected from each added element group consisting of the added elements A (Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg, B, Al, Ga, In, Tl) or the added elements B (N, P, As, Sb, Bi, O, S, Se, Te) are contained.

【Claim 7】 A method for manufacturing the thermoelectric conversion material, including a step of laminating a silicon layer or a silicon-rich layer composed mainly of silicon and an added element-rich layer composed mainly of one or more added elements to make a silicon a p-type or n-type semiconductor on a substrate or a film, forming a laminate and making the entire composition of the laminate to be a silicon-based material containing said added element in an amount of 0.001 to 20 at%.

【Claim 8】 The method for manufacturing the thermoelectric conversion material according to claim 1, wherein a heat treatment is performed on a laminate after lamination.

【Detailed Description of the Invention】

【0001】

【Technical Field of the Invention】

This invention relates to a novel thermoelectric conversion material in which a silicon is made to contain various types of added elements at an amount of 20 at% or less, and more particularly relates to a polycrystal silicon-based thermoelectric conversion material of a thin film form, characterized in that a silicon-rich layer composed mainly of silicon and an added element composed mainly of an added element are film-formed and laminated on the required substrate such as silicon and glass, and heat-treated, and a structure in which an added element-rich

phase is dispersed at the grain boundary of a silicon-rich phase in the lamination direction and/or in each layer is produced, the result of which is an extremely large Seebeck coefficient and low thermal conductivity, allowing the thermoelectric conversion efficiency to be raised dramatically, and a silicon, which is an abundant resource, is a main component and environmental pollution is extremely little.

【0002】

【Background Art】

Thermoelectric conversion elements are devices that are expected to see practical use because of their efficient utilization of the high levels of thermal energy required in recent industrial fields. An extremely broad range of applications have been investigated, such as a system for converting waste heat into electrical energy, small, portable electric generators for easily obtaining electricity outdoors, flame sensors for gas equipment, and so forth.

【0003】

This conversion efficiency from thermal energy to electrical energy is a function of the Figure of merit  $ZT$ , and rises in proportion to  $ZT$ . This Figure of merit  $ZT$  is expressed by Formula 1.

$$ZT = \frac{\alpha^2 \sigma T}{\kappa}$$

Formula 1

Here,  $\alpha$  is the Seebeck coefficient of the



thermoelectric material,  $\alpha$  is the electrical conductivity,  $\kappa$  is the thermal conductivity, and  $T$  is the absolute temperature expressed as the average value for the thermoelectric element on the high temperature side ( $T_H$ ) and the low temperature side ( $T_L$ ).

【0004】

Silicides such as  $\text{FeSi}_2$  and  $\text{SiGe}$ , which are thermoelectric conversion materials that have been known up to now, are abundant natural resources, but the former has a Figure of merit  $ZT$  of 0.2 or less, its conversion efficiency is low, and its usable temperature range is extremely narrow, while no decrease in thermal conductivity is seen with the latter unless the germanium content is about 20 to 30 at%, and germanium is a scarce resource. Also, silicon and germanium have a state in which there is a broad liquidus and solidus for complete solid solution, and it is difficult to produce a uniform composition with melting or ZL (zone leveling), to impede industrial application. For these reasons, the above-mentioned materials have not found widespread use.

【0005】

The thermoelectric materials with the highest Figure of merit at the present time are  $\text{IrSb}_3$ , having a skutterudite-type crystal structure, and  $\text{BiTe}$ ,  $\text{PbTe}$ , and other such chalcogen compounds, which are known to provide highly efficient thermoelectric conversion capability, but

from the standpoint of protecting the global environment, the use of these heavy metal elements is expected to be restricted in the future.

【0006】

【Problems to be solved by the Invention】

Silicon, meanwhile, has a high Seebeck coefficient, but has extremely high thermal conductivity, and is therefore not considered suitable as a high efficiency thermoelectric material, and research into the thermoelectric characteristics thereof has been limited to silicon with a carrier concentration of  $10^{18}(\text{Mm}^3)$  or less.

【0007】

The inventors discovered that doping silicon single piece with various elements, such as doping silicon with both a trace amount of a Group III element or Group V element and a small amount of germanium, makes it possible to lower thermal conductivity, and the Seebeck coefficient will be equivalent to or better than that of conventional Si-Ge and Fe-Si compounds, or will be extremely high at a given carrier concentration. They also discovered that this material exhibits a good Figure of merit as a thermoelectric conversion material, without losing the fundamental advantages afforded by silicon single piece, and can improve the performance.

【0008】

The inventors also produced p- and n-type

semiconductors by doping a silicon with various elements, and examined the relationship of the doping amount to the thermoelectric characteristics, and as a result found that up to an added amount (that is, a carrier concentration) of  $10^{18}(\text{M}/\text{m}^3)$ , the Seebeck coefficient decreases in inverse proportion to the carrier concentration, but has a maximum value from  $10^{18}$  to  $10^{19}(\text{M}/\text{m}^3)$ .

【0009】

It is an object of the present invention to provide a polycrystal silicon-based thermoelectric conversion material composed of a construction easy to manufacture or of a construction easy to manufacture by the same manufacturing method as that of an integrated circuit, and its manufacturing method, without sacrificing the high Seebeck coefficient and electrical conductivity had by this novel silicon-based thermoelectric conversion material discovered by the inventors.

【0010】

【Means to solve the Problems】

The inventors diligently examined the mechanism by which a high Seebeck coefficient is obtained with a silicon-based thermoelectric conversion material doped with various elements, whereupon they learned that this novel silicon-based material has a structure in which at the grain boundary of a silicon-rich phase containing mainly silicon, the concerned added element-rich phase is formed as shown

in Figure 3.

【0011】

The inventors also investigated a crystal structure, and they discovered that since the added element cohesion occurs at the crystal grain boundary and the conduction of carriers can be increased, a high Seebeck coefficient is obtained in the silicon-rich phase within the crystal grain. As a method for keeping the Seebeck coefficient high and lowering the thermal conductivity, they investigated the controlling of the crystal structures other than the component-based and found that a structure in which if the cooling rate is controlled during melting and solidification, the silicon-rich phase and added element-rich phase will be dispersed in the required arrangement within the material can be obtained.

【0012】

Then, the inventors sharply investigated a construction and a manufacturing method which can realize simply a silicon-based thermoelectric conversion material having such a structure and constitution. As the result, they found that a silicon or a silicon-rich layer composed mainly of a silicon and an added element-rich layer are film-formed and laminated, for example, alternately and then heat-treated, by which the same structure as that of Figure 3 can be obtained in a laminating thickness direction or per each layer, and further, by film-forming and laminating

a silicon-rich layer of a silicon and the required added element and an added element-rich layer composed chiefly of the required added element and containing also a silicon alternately, the same construction as the structure obtained by controlling the cooling rate during melting and solidification can be obtained and said material having a high Figure of merit can be obtained by just a simple method of film-forming on a substrate, and accomplished this invention.

【0013】

【Mode of Working of the Invention】

The structure in which the above-mentioned added element-rich phase is formed at the grain boundary of the silicon-rich phase composed mainly of silicon, which is a characteristic feature of the thermoelectric conversion material of the present invention, will now be described. For example,  $\text{Si}_{1-x}\text{Ge}_x$  melts (at%) were produced by arc melting, and the cooling after melting must be performed by quenching. As shown in a schematic diagram of Figure 2, the structure is a structure in which are formed a silicon-rich phase consisting of silicon alone or almost entire of silicon but including an added element and an added element-rich phase in which an added element is segregated at the grain boundary of this silicon-rich phase.

【0014】

The relationship between carrier concentration of an

n-type and p-type silicon and the state of crystal grain boundary deposition of an added element of phosphorus or boron instead of germanium was examined, which confirmed that the correlation of the carrier concentration and the doping amount increased agreeably. Because of the structure in which said added element-rich phase was formed at the grain boundary of the silicon-rich phase, the added element was clumped at the crystal grain boundary, the electrical conductivity resulting from carriers was high, a high Seebeck coefficient was obtained in the silicon-rich phase within the crystal grains.

【0015】

Furthermore, it was confirmed that the thermal conductivity of this silicon-based thermoelectric conversion material decreases as the carrier concentration is increased. This is believed to be because  $\kappa_{ph}$  was decreased by local phonon scattering of impurities resulting from the added element in the crystals.

【0016】

The thermoelectric conversion material of the present invention can make use of a monocrystalline or polycrystalline silicon substrate, a glass or ceramic substrate, a resin substrate, or the like, or a resin film, or any known substrate or film that can be utilized in the formation of a thermoelectric conversion element, for instance, over another film. The structure is characterized

in that a silicon layer or a silicon-rich layer composed mainly of silicon and an added element-rich layer having as its main component one or more added elements to make a p-type and n-type semiconductor are laminated over one of these substrates or films. In other words, a laminate of a silicon layer or a silicon-rich layer and an added element-rich layer are formed on a substrate.

【0017】

For instance, the structural example shown in Figure 1A is such that first a thin film layer of germanium and phosphorus is formed in the required thickness as the added element-rich layer over a monocrystalline silicon substrate with a crystal plane of (111) or (100), then a thin film layer of just silicon is formed in the required thickness as the silicon-rich layer, and the above-mentioned thin film layers of germanium and phosphorus and thin film layers of silicon are alternately laminated.

【0018】

If a heat treatment (1 hour at 873K in a vacuum, for example) is conducted after lamination, then as shown in Figure 1B, there will be diffusion between the thin film layers, resulting in a laminate in which thin film layers of  $\text{Ge} + \text{P} + \Delta \text{Si}$  into which silicon has diffused are alternately laminated with thin film layers of  $\text{Si} + \Delta \text{P} + \Delta \text{Ge}$  into which germanium and phosphorus have diffused. When the silicon-rich layer in Figure 1A is an  $\text{Si} + \text{P}$  thin

film layer, the Si + P layer will become an Si +  $\Delta$ Ge + P layer after heat treatment.

【0019】

Also, as shown in Figure 2, the heat treated lamination state of Figure 1B can be achieved by forming a thin film layer of Ge + P + Si (made up primarily of germanium and phosphorus, but including silicon as well; used as the an added element-rich layer) in the required thickness, then forming a thin film layer of Si + Ge (used as the silicon-rich layer) in the required thickness, and then alternately laminating these Ge + P + Si thin film layers and Si + Ge thin film layers.

【0020】

The laminate shown in Figure 1B or Figure 2, formed by lamination over a monocrystalline silicon substrate, is equivalent to the structure shown in Figure 3, in which a silicon-rich phase consisting primarily of silicon and an added element-rich phase in which an added element has become segregated at the grain boundary of this silicon-rich phase are formed in the thickness direction (that is, the lamination direction), and when a diffusion heat treatment is performed, the resulting structure is similar in the plan view of the various thin film layers. This laminate is a thermoelectric conversion material having a structure equivalent to that in Figure 3, which was obtained by quenching a silicon-based melt containing the required



amounts of germanium and phosphorus.

【0021】

Therefore, as to the thickness of the above-mentioned silicon layers or silicon-rich layers and added element-rich layers, and the lamination thickness ratio thereof, the composition and thickness of the silicon-rich layers and the added element-rich layers must be selected according to the composition of the targeted silicon-based thermoelectric conversion material so that these are suitably dispersed, and any lamination means can be employed as long as the structure shown in Figure 3 can at least be achieved in the lamination direction. Examples include varying the composition of the silicon-rich layers and the added element-rich layers for each lamination, and combining a variety of compositions or using various patterns in which the lamination pattern is not merely alternating as above.

【0022】

A thermoelectric conversion material in which films are formed and laminated over a substrate as above is suitably designed so the composition discussed below will be achieved for the laminate as a whole, and the structure shown in Figure 3 is formed in the lamination direction, so a thermoelectric conversion element can be easily obtained by forming and laminating p- and n-type semiconductors, electrode films, and the like from this silicon-based

thermoelectric conversion material in a suitable pattern so that the temperature gradient direction of the targeted thermoelectric conversion element will be the above-mentioned lamination direction.

【0023】

The film formation and lamination can be accomplished by any known growth or film formation means, such as vapor deposition, sputtering, CVD, or another such vapor phase growth method, discharge plasma treatment, or plasma treatment using a gas containing an added element. Also, as will be discussed below, any element can be added as the added element, so a variety of cases are conceivable, including those in which any means can be selected and those in which the means is limited by the type of element in question. In addition, the treatment conditions for the selected means will vary considerably with the combination of elements when two or more are used, so the above-mentioned means and conditions must be appropriately selected according to the targeted composition. As for the heat treatment, any temperature conditions, atmosphere, and heating method can be employed as long as the conditions result in the desired diffusion between the layers.

【0024】

A thermoelectric conversion material according to the present invention is a highly efficient silicon-based thermoelectric conversion material of a p-type and n-type

semiconductor which lowers the electric resistance, improves the Seebeck coefficient and improves dramatically Figure of merit without losing the fundamental advantages afforded by silicon single piece by adding various impurities into the polycrystalline silicon semiconductor having a diamond-like crystal structure and adjusting the carrier concentration.

【0025】

When the applications of a thermoelectric conversion material are considered, emphasis must be placed on one of the characteristics, such as the Seebeck coefficient, electrical conductivity, or thermal conductivity depending on the conditions which vary with the application, such as the heat source, where and how the material is used, and the size of the current and voltage to be handled, but the thermoelectric conversion material of the present invention allows the carrier concentration to be determined by means of the added amount of the selected added element.

【0026】

For example, when one or more elements from the above-mentioned added elements  $\alpha$  are contained in an amount of 0.001 to 0.5 at%, a p-type semiconductor with a carrier concentration of  $10^{17}$  to  $10^{20}$  (M/m<sup>3</sup>) will be obtained, and when added elements  $\alpha$  are contained in an amount of 0.5 to 5.0 at%, a p-type semiconductor with a carrier concentration of  $10^{19}$  to  $10^{21}$  (M/m<sup>3</sup>) will be

obtained.

【0027】

Similarly, when one or more elements from the above-mentioned added elements  $\beta$  are contained in an amount of 0.001 to 0.5 at%, an n-type semiconductor with a carrier concentration of  $10^{17}$  to  $10^{20}$  ( $M/m^3$ ) will be obtained, and when added elements  $\beta$  are contained in an amount of 0.5 to 10 at%, an n-type semiconductor with a carrier concentration of  $10^{19}$  to  $10^{21}$  ( $M/m^3$ ) will be obtained.

【0028】

When the above-mentioned added elements  $\alpha$  or added elements  $\beta$  are contained in an amount of 0.5 to 5.0 at% so that the carrier concentration is  $10^{19}$  to  $10^{21}$  ( $M/m^3$ ), a highly efficient thermoelectric conversion element is obtained, and the thermoelectric conversion efficiency is excellent, but the thermal conductivity thereof is about 50 to 150 W/m · K at room temperature, and if the thermal conductivity could be decreased, there would be a further improvement in the Figure of merit ZT.

【0029】

Generally, the thermal conductivity of solids is given as a sum of the conduction due to phonon and the conduction due to carrier. In case of thermoelectric conversion material of a silicon-based semiconductor, since the carrier concentration is small, the conduction due to phonon is dominant. Therefore, to decrease the thermal

conductivity, it is necessary to make the absorption or scattering of phonon large. In order to make the absorption or scattering of phone large, it is effective to disturb the regularity of the crystal structure, and the crystal grain size.

【0030】

Then, as the results of various studies about added elements to silicon, it is possible to disturb the crystal structure without changing the carrier concentration in silicon by adding at least one Group III element and at least one Group V element to silicon and controlling the carrier concentration to a range of  $10^{19}$  to  $10^{21}$  (M/m<sup>3</sup>). It is found that the thermal conductivity can decrease 30 to 90%, to 150 W/m · K or less at room temperature, and a high efficiency thermoelectric conversion material can be obtained.

【0031】

Further, in the above constructed thermoelectric conversion material, a p-type semiconductor will be obtained if the Group III element is contained in an amount 0.3 to 5 at% larger than the Group V element, and an n-type semiconductor will be obtained if the Group V element is contained in an amount 0.3 to 5 at% larger than the Group III element.

【0032】

The inventors also investigated whether a decrease

in thermal conductivity could be achieved with something other than Group III elements and Group V elements, and found that the crystal structure can be disturbed without changing the carrier concentration in the silicon, the thermal conductivity can be brought below 150 W/m · K or less at room temperature, and a highly efficient thermoelectric conversion material can be obtained by adding a Group III - V compound semiconductor or a Group II - VI compound semiconductor to silicon, further adding at least one type of Group III element or Group V element and controlling the carrier concentration to a range of  $10^{19}$  to  $10^{21}$  (M/m<sup>3</sup>).

【0033】

Furthermore, as a result of variously investigating other added elements to silicon, the inventors found that if the silicon contains the Group IV elements germanium, carbon, and tin in an amount of 0.1 to 5 at%, and some of the silicon elements are replaced with a Group IV element with a different atomic weight, there will be greater phonon scattering in the crystals and the thermal conductivity of the semiconductor can be reduced 20 to 90%, to 150W/m · K or less at room temperature. Further, it is possible to obtain a thermoelectric conversion material wherein a p-type semiconductor is obtained if the Group III element is contained in an amount of 0.1 to 5.0 at% and furthermore a thermoelectric conversion material wherein an

n-type semiconductor is obtained if the Group V element is contained in an amount of 0.1 to 10 at%.

【0034】

Other elements besides the above-mentioned Group III and V elements were examined to see if they could similarly be added to silicon in the thermoelectric conversion material of the present invention, whereupon it was confirmed that while there are no particular restrictions as long as a p- or n-type semiconductor will result, if elements whose ion radii are too different are used, almost all will precipitate in the grain boundary phase, so it is preferable to use an element whose ion radius is relatively close to that of silicon. It is confirmed that one or more elements of the following groups are particularly effective as added elements  $\alpha$  to make a p-type semiconductor or as added elements  $\beta$  to make an n-type semiconductor.

【0035】

The added element  $\alpha$  are each group consisting of added elements A (Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg, B, Al, Ga, In, Tl) and transition metal elements  $M_1$  (Y, Mo, Zr). The added elements  $\beta$  are each group consisting of added elements B (N, P, As, Sb, Bi, O, S, Se, Te), transition metal elements  $M_2$  (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Ru, Rh, Pd, Ag, Hf, Ta, W, Re, Os, Ir, Pt, Au; where Fe accounts for 10 at% or less), and rare earth elements RE (La, Ce, Pr, Nd,

Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu).

【0036】

Further, if, in added elements  $\alpha$  to make a p-type semiconductor and added elements  $\beta$  to make an n-type semiconductor, at least one type from each group is contained at an amount of 0.002 to 20 at% in total amounts, for example, if in order to obtain a p-type semiconductor the total amount of added elements  $\alpha$  is contained only at the required amount to make a p-type semiconductor over that of added elements  $\beta$ , voluntary combinations of each group can be selected.

【0037】

【Examples】

Example 1

A silicon (111) wafer was put in a vacuum chamber at  $10^{-6}$  Torr, the elements shown in Table 1 were formed by electron beam heating alternately as layer A and layer B for 50 laminations in the thicknesses shown in Table 1.

【0038】

The samples on the silicon wafers thus obtained were cut to sizes of  $5 \times 15$  mm,  $10 \times 10$  mm, and 10 mm (outside diameter), and the Seebeck coefficient, Hall coefficient (including carrier concentration and electrical conductivity), and thermal conductivity of each were measured along with the silicon wafer. Table 2 shows the measured values at 1100K and the Figure of merit ( $ZT = S^2T/$



$\rho$   $\kappa$  ).

【0039】

The temperature differential between the high and low temperature portions during temperature elevation was set to be about 6K, the thermoelectromotive force of the samples was measured with a digital multimeter, and this value was divided by the temperature differential to find the Seebeck coefficient. The Hall coefficient was measured by AC method, and the electrical resistance was measured by four-terminal method simultaneously with the carrier concentration. The thermal conductivity was measured by laser flash method.

【0040】

Example 2

A silicon (111) wafer substrate was put in a vacuum chamber at  $10^{-2}$  Torr, the elements shown in Table 3 were film-formed by sputtering alternately as layer A and layer B for 50 laminations in the thicknesses shown in Table 1.

【0041】

The samples on the silicon wafers thus obtained were cut to sizes of  $5 \times 15$  mm,  $10 \times 10$  mm, and 10 mm (outside diameter), and the Seebeck coefficient, Hall coefficient (including carrier concentration and electrical conductivity), and thermal conductivity of each were measured along with the silicon wafer. Table 4 shows the measured values at 1100K and the Figure of merit ( $ZT = S^2T/$

$\rho, \kappa$ ).

【0042】

【Table 1】

No.	Composition of layer A	Layer A thickness (nm)	Composition of layer B	Layer B thickness (nm)	Cycles (times)	Heating temp. (K)	Heating time (h)
1	Si	20	B	1	50	873	1
2	Si	50	B	3	50	873	1
3	Si	50	Al	3	50	873	1
4	Si	20	Ge <sub>0.9</sub> B <sub>0.1</sub>	1	50	873	1
5	Si	50	Ge <sub>0.9</sub> B <sub>0.1</sub>	3	50	873	1
6	Si	50	Ge <sub>0.8</sub> Ca <sub>0.2</sub>	3	50	873	1
7	Si	20	P	2	50	873	1
8	Si	50	P	5	50	873	1
9	Si	50	As	5	50	873	1
10	Si	20	Ge <sub>0.8</sub> P <sub>0.2</sub>	2	50	873	1
11	Si	50	Ge <sub>0.8</sub> P <sub>0.2</sub>	5	50	873	1
12	Si	50	Ge <sub>0.8</sub> Sb <sub>0.2</sub>	5	50	873	1

【0043】

【Table 2】

No.	Seebeck coefficient (mV/K)	Electrical resistivity $\times 10^{-5}$ ( $\Omega \cdot m$ )	Thermal conductivity (W/m · K)	Figure of merit (ZT)
1	0.273	1.51	21	0.26
2	0.264	1.47	24	0.22
3	0.241	1.75	29	0.13
4	0.278	1.59	7	0.76
5	0.276	1.49	8	0.70
6	0.295	1.82	8	0.66
7	-0.309	1.62	19	0.34
8	-0.306	1.53	21	0.32
9	-0.300	1.64	28	0.22
10	-0.316	1.57	7	1.00
11	-0.312	1.53	8	0.87
12	-0.334	1.67	8	0.92

【0044】

【Table 3】

No.	Composition of layer A	Layer A thickness (nm)	Composition of layer B	Layer B thickness (nm)	Cycles (times)	Heating temp. (K)	Heating time (h)
21	Si	20	B	1	50	873	1
22	Si	50	B	3	50	873	1
23	Si	50	Al	3	50	873	1
24	Si <sub>0.9</sub> Ge <sub>0.1</sub>	20	B	1	50	873	1
25	Si <sub>0.9</sub> Ge <sub>0.1</sub>	50	B	3	50	873	1
26	Si <sub>0.9</sub> Ge <sub>0.1</sub>	50	Ga	3	50	873	1
27	Si	20	P	2	50	873	1
28	Si	50	P	5	50	873	1
29	Si	50	As	5	50	873	1
30	Si <sub>0.9</sub> Ge <sub>0.1</sub>	20	P	2	50	873	1
31	Si <sub>0.9</sub> Ge <sub>0.1</sub>	50	P	5	50	873	1
32	Si <sub>0.9</sub> Ge <sub>0.1</sub>	50	Sb	5	50	873	1

【0045】

【Table 4】

No.	Seebeck coefficient (mV/K)	Electrical resistivity $\times 10^{-5}$ ( $\Omega \cdot m$ )	Thermal conductivity (W/m · K)	Figure of merit (ZT)
21	0.269	1.41	23	0.25
22	0.261	1.37	25	0.22
23	0.237	1.64	30	0.13
24	0.272	1.49	8	0.68
25	0.270	1.40	9	0.64
26	0.290	1.72	9	0.60
27	-0.301	1.52	21	0.31
28	-0.299	1.43	23	0.30
29	-0.294	1.54	29	0.21
30	-0.311	1.47	8	0.90
31	-0.306	1.43	9	0.80
32	-0.328	1.57	9	0.84

【0046】

【Effects of the Invention】

Silicon, the main component of the thermoelectric conversion material of the present invention, is an outstanding material in terms of protecting the global environment and conserving the earth's resources, and also affords excellent safety. Furthermore, it is light (has a low specific gravity), which makes it very favorable for thermoelectric conversion elements used in automobiles. Silicon also has good corrosion resistance, which is an advantage in that no surface treatment or the like is needed.

【0047】

Because it makes use of silicon as its main component, the thermoelectric conversion material of the present invention is less expensive than Si-Ge-based materials containing large quantities of costly germanium, and provides a higher Figure of merit than Fe-Si-based materials. Furthermore, the silicon used in the present invention is much lower in purity than that used in semiconductor devices, so the raw material is available at relatively low cost, and the production can be performed just by a simple method for film-forming and laminating, the result of which is a thermoelectric conversion material with good productivity, stable quality, and low cost.

【0048】

The thermoelectric conversion material of the present invention takes full advantage of the characteristics of silicon, namely, its low electrical resistance and large Seebeck coefficient despite having a large carrier concentration, and also greatly ameliorates its drawback of high thermal conductivity, and is therefore an effective way to obtain a material with a high Figure of merit. Another advantage is that the properties can be controlled by means of the type and amount of added elements.

**【Brief Explanation of Drawings】**

**【Fig. 1】**

Fig. 1 is a schematic diagram illustrating the state of lamination of the thermoelectric conversion material of the present invention, where A shows the state after lamination, and B shows the state after heat-treating.

**【Fig. 2】**

Fig. 2 is a schematic diagram illustrating the another state of lamination of the thermoelectric conversion material of the present invention.

**【Fig. 3】**

Fig. 3 is a schematic diagram illustrating the crystal structure of the thermoelectric conversion material of the present invention.

**【Name of Document】** Summary

**【Summary】**

**【Objects】** It is to provide a polycrystal silicon-based thermoelectric conversion material and a method for manufacturing the same, having a structure which can be easily manufactured or can easily manufactured by the same method as the manufacturing method of an integrated circuit, without sacrificing the high Seebeck coefficient and electrical conductivity had by the novel silicon-based thermoelectric conversion material material containing various added elements in an amount of 20 at% or less in silicon.

**【Means for solving】** By film-forming and laminating a silicon-rich layer composed mainly of silicon and an added element-rich element composed chiefly of an added element on the required substrate of silicon or glass, etc., heat-treating and producing a structure in which an added element-rich layer is dispersed at the grain boundary of a silicon-rich phase in the lamination direction and/or in each layer, it is possible to obtain a polycrystal silicon-based thermoelectric conversion material of a thin film form in which Seebeck coefficient is extremely large, the thermal conductivity becomes low, the thermoelectric conversion efficiency is dramatically improved, a silicon, which is an abundant resource, is a main component and the environmental pollution is extremely little.



**【Selected Figure】** Fig. 1

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出 願 年 月 日  
Date of Application: 1999年 3月10日

願 番 号  
Application Number: 平成11年特許願第063099号  
T. 10/C]: [JP1999-063099]

願 人  
Applicant(s): 株式会社NEOMAX

2004年 5月 7日

特許庁長官  
Commissioner,  
Japan Patent Office

今 井 康 夫

